

# Studies on the Reaction of Coal with Ethoxycarbonylcarbene

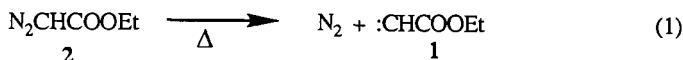
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## Introduction

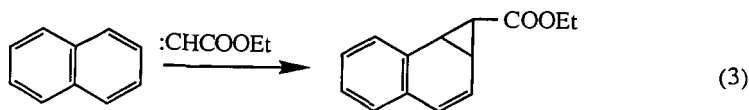
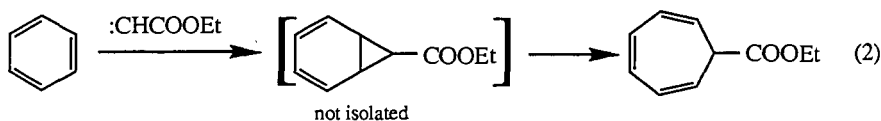
Studies of the molecular structure of coal have relied heavily on the chemical reactions of the coal and on the structure of the products produced. Many of these reactions involve high temperatures and fairly severe conditions, and, as a result, it is frequently difficult to relate the reaction products to coal structure because of molecular rearrangements and unanticipated reactions. For this reason people have sought mild reactions which would depolymerize the coal and provide tractable, identifiable products. Among these are oxidations using trifluoroperoxyacetic acid (1),  $\text{Na}_2\text{Cr}_2\text{O}_7$  (2),  $\text{Ag}_2\text{O}$  (3),  $\text{HNO}_3$  (4) and  $\text{H}_2\text{O}_2$  (5), and alkylation (6). Most other attempts at depolymerization involve high temperatures and much more severe conditions (7).

In this report we examine the reactions of coal with ethoxycarbonylcarbene (1) formed by the mild thermal decomposition of ethyl diazoacetate (2; eqn. 1). There are a few reports in the literature of



studies involving reaction of coal with diazo compounds or carbenes. All but one have involved the use of diazomethane to analyze for  $\text{-COOH}$  and phenolic  $\text{OH}$  groups (8,9) and these studies have shown that it is a rather poor analytical method. One recent study (9) reports on the reaction of labeled  $^{14}\text{CH}_2\text{N}_2$  and  $^{14}\text{CCl}_2$  with coal and coal-derived materials. The conclusions, based strictly on the uptake of reagent both before and after exposure to air, were that air exposed fractions exhibited more ketonic and carboxyl groups at the expense of phenolic hydroxyl, benzylic methylenes and other oxidizable moieties.

The reactions of carbenes, particularly ethoxycarbonyl carbene (1), with a very large variety of organic compounds is quite well known (10). They will add to aromatic molecules to form 3-membered and 7-membered rings, they will insert into  $\text{C-H}$  bonds, will react with some heteroatoms and will undergo various free radical reactions. Equations 2 and 3 illustrate the first of these reactions by showing the reaction of the carbene 1 with benzene and naphthalene respectively.



In this paper we report on the reactions of 1 (prepared by mild thermal decomposition of 2) with an Illinois No. 6 HVCB bituminous coal (PSOC-1351) and studies of the products involving thermal

analyses (TGA, DTA), diffuse reflectance FT-IR spectroscopy (DRIFT), and some preliminary GC analyses.

## Results and Discussion

A sample of Illinois No. 6 HVCB bituminous coal obtained from the Pennsylvania State University Coal Research Section (PSOC-1351) was crushed to <100 mesh under argon, dried at 120-125°C, and then treated with ethyl diazoacetate (**2**) in pentane. The mixture was stirred overnight at room temperature, under N<sub>2</sub>, the pentane was removed in vacuum and the coal/**2** mixture was slowly heated to 100°C until nitrogen evolution ceased. The temperature was then raised to 120°C for an additional 30 minutes to insure complete decomposition of **2**. After weighing, a portion of the samples was extracted (Soxhlet) for 24 hours with toluene/methanol (9:1), and the extract was concentrated by distillation.

The above procedure was run using 1, 2 and 3 grams of **2** to 1 g of coal and, in addition, a control experiment, using the coal but omitting **2**, was run. (The runs were called Coal 1, 2, 3 and 0 respectively.) Further, a control experiment without the coal (monitored by <sup>1</sup>H NMR spectroscopy) showed that **2** was stable to the overnight stirring procedure. Table 1 shows the results. It should be noted that the decomposition of **2** apparently begins below 80°C and N<sub>2</sub> evolution is fairly vigorous at 80°. This suggests that, since ethyl diazoacetate normally requires higher temperatures for decomposition (10), the reaction is being catalyzed, presumably by the mineral matter in the coal. It is also well known that catalyzed decomposition of **2** gives rise to carbene products (10).

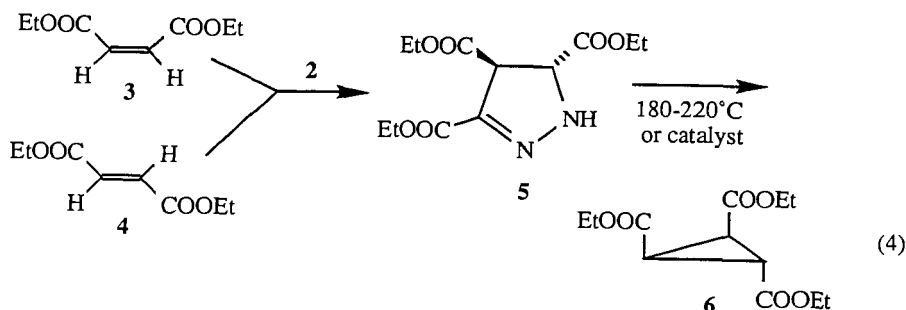
Table 1. Results of the Reaction of N<sub>2</sub>CHCOOEt (**2**) with Illinois No. 6 Coal

|                                 | Coal 0 | Coal 1 | Coal 2 | Coal 3 |
|---------------------------------|--------|--------|--------|--------|
| <b>2</b> (g)                    | 0      | 1.016  | 2.028  | 3.000  |
| coal (g)                        | 1.004  | 1.002  | 1.010  | 1.015  |
| Amt. recovered (g) <sup>a</sup> | 1.015  | 1.563  | 2.264  | 2.654  |
| % yield <sup>b</sup>            | 101    | 88     | 89     | 81     |
| % extracted                     | 31     | 45     | 63     | 71     |

a) Weight after heating and loss of N<sub>2</sub>.

b) Calculated based on weight of coal and carbene **1**.

In order to be sure that the major reactions were of the carbene, **1**, with the coal, we independently prepared the known products formed when **2** decomposes by itself and when **2** reacts with the dimers of **1**. The dimers, namely, diethyl maleate (**3**) and diethyl fumarate (**4**) are known to give the pyrazoline, **5**, on reaction with **2**, and this, in turn, thermally (above 180°C) or catalytically is known to decompose to cyclopropane, **6** (equation 4) (10-12). Capillary gas chromatographic analysis of the concentrated extracts showed small amounts of **3-6** in coal 1 (about 8 area percent total of the non-solvent peaks eluting from the column), a little more of these in coal 2 (ca. 10%) and a bit more in coal 3 (ca. 13%). Also, since **5** does not produce **6** below 180°C except by catalysis with metal ions (12), we must conclude that the reaction **5** → **6** was catalyzed in the coal. It was thus clear that the major reaction of the species **1** and **2** was with the coal.



In addition to the peaks corresponding to 3-6 there were, of course, many other peaks in the GC of the extracts. The number of peaks in coal 3 was about the same as in coal 2 while in coal 1 the number was smaller and was smallest in coal 0. Work is in progress to try to identify these peaks, or at least the major ones.

Table 2 shows the results of thermogravimetric analyses (TGA) giving weight loss between 200° and 600°C for the coal samples before extraction. It should be noted that carbene treatment increased the amount of material which is volatile below 600°C by a factor of 2 to 3, a rather significant increase. Also, the major effect is shown on going from coal 0 to coal 1 and 2 while a smaller effect is shown on going from coal 2 to 3. The derivative plots (DTA) show the maximum rate of weight loss for coal 0 (2.0%/min) at 470°C, for coal 1 (6.2%/min) at 260°C, and for coal 2 (9.1%/min) at about 260°C. Coal 3 is essentially the same as coal 2. It is thus clear that in addition to increasing the amount of material which can be volatilized below 600°C, carbene treatment also lowers very substantially the temperature of maximum decomposition. Also, since the TGA curves change substantially in the carbene treated coals compared with the control, coal 0, the diazo compound (2) and hence the carbenes must be getting into the interior pores of the coal and giving rise to reaction. Thus we are not looking simply at a surface reaction.

Table 2. Results of Thermogravimetric Analysis

|                              | Coal 0   | Coal 1   | Coal 2   | Coal 3   |
|------------------------------|----------|----------|----------|----------|
| % weight loss <sup>a,b</sup> | 21 ± 1.0 | 45 ± 1.5 | 57 ± 2.1 | 63 ± 1.9 |

a) % weight loss between 200° and 600°C.

b) Average of 5 separate runs each.

Finally, diffuse reflectance FT-IR (DRIFT) spectra were obtained for the various samples. There were several differences observable upon carbene treatment. First, and most trivial, is that an ester carbonyl appeared at 1736 cm<sup>-1</sup> in all samples. More significantly, a small peak at about 3050 cm<sup>-1</sup>, which is presumably due to aromatic C-H (13,14), disappeared with increasing amount of 2. A new

aliphatic CH peak appeared at  $2962\text{ cm}^{-1}$  while a substantial aromatic peak at  $1610\text{ cm}^{-1}$  (13,14) in coal 0 got much smaller in coal 1 and disappeared in coals 2 and 3. A peak at  $856\text{ cm}^{-1}$  appeared with carbene treatment and a smaller one at  $771\text{ cm}^{-1}$  also grew in. One or both of these could be due to alkene C-H out of plane deformations which occur in this region (13).

One area that also merits notice is the  $400\text{--}550\text{ cm}^{-1}$  region. According to Solomon (15) and references cited in this publication, this region is due to metal-sulfur and metal-oxygen bonds in the minerals of the coal. In the present study the  $546\text{ cm}^{-1}$  peak progressively disappeared in going from coal 0 to coal 3 and the  $475\text{ cm}^{-1}$  peak also got smaller. This is consistent with the suggestion that the diazo compound decomposition was catalyzed and the reaction of the minerals with the ethyl diazoacetate (2) caused these absorptions to vanish.

## Summary

Ethoxycarbonylcarbene (1) produced by the mild thermal decomposition of ethyl diazoacetate (2) has been reacted with Illinois No. 6 coal. Thermal analysis has shown that the treated coal is considerably more volatile than untreated coal and that the temperature of maximum volatility is significantly reduced. Infrared studies have shown that, in addition to the appearance of ester carbonyl absorption in the treated samples, there were also peaks attributable to aromatic rings and to mineral matter which diminish and peaks attributable to alkenes which also appeared. This is consistent with the known reactions of ethyl diazoacetate and ethoxycarbonylcarbene (10).

## Experimental Section

**General.** Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Capillary GC was on a Varian model 3700 gas chromatograph using a  $0.315\text{ mm} \times 30\text{ m}$  DB-5+ column with injector temperature at  $250^\circ\text{C}$ , FID detector at  $300^\circ\text{C}$ , and temperature programmed at  $10^\circ\text{C}/\text{min}$  from an initial temperature of  $60^\circ\text{C}$  (held for 5 min) to a final temperature of  $270^\circ\text{C}$ . Diffuse reflectance FT-IR was carried out on a Biorad-Digilab FTS-40 instrument equipped with a TGS detector and a Barnes Analytical-Spectra Tech diffuse reflectance accessory. The samples were 2 mg of coal and 100 mg of KBr. Thermal analyses were done on a DuPont system including a model 1090 thermal analyzer, 951 thermogravimetric analyzer and 1091 microprocessor.  $^1\text{H}$  NMR spectra were obtained on a Varian T-60 60 MHz spectrometer.

**Materials.** Illinois No. 6 HVCB bituminous coal was obtained from the Pennsylvania State University Coal Research Section (PSOC-1351), and was reported to have the following elemental analysis: (wt. %-dry) C = 67.33%; H = 4.11%; N = 1.17%; organic S = 2.93%; O = 10.74%; and mineral matter 13.72%. The proximate analysis: ash = 11.49%; volatile matter = 40.34% and fixed carbon 48.17%. Pentane was stirred with several portions of  $\text{H}_2\text{SO}_4$  until there was no color produced, with 0.5 N  $\text{KMnO}_4$  in 3 M  $\text{H}_2\text{SO}_4$  for 12 hr., washed with  $\text{H}_2\text{O}$  and then aqueous  $\text{NaHCO}_3$  and dried with  $\text{MgSO}_4$ . It was distilled through a 12 in. Heli-pak column and the fraction boiling  $35\text{--}36^\circ\text{C}$  was collected and stored over  $4\text{ \AA}$  molecular sieves. Ethyl diazoacetate was prepared from ethyl glycinate hydrochloride and distilled, b.p.  $24\text{--}26^\circ\text{C}/1.5\text{ torr}$  (16). Methanol was distilled through a 12 in. Heli-pak column and the fraction b.p.  $64.0\text{--}64.5^\circ\text{C}$  was collected and stored over  $4\text{ \AA}$  molecular sieves. Toluene was distilled through a 12 in. Heli-pak column and the fraction b.p.  $110\text{--}110.5^\circ\text{C}$  was collected and stored over  $4\text{ \AA}$  molecular sieves.

**Reaction of Coal with Ethyl Diazoacetate.** The Illinois No. 6 coal was crushed under argon to pass through a 100 mesh screen and dried at  $120\text{--}125^\circ\text{C}$  for 3 hr. under  $\text{N}_2$ . After cooling for 30 min., 1 g portions of coal were put into 100 mL round-bottomed flasks into which was put 10 mL of pentane and the ethyl diazoacetate (none for coal 0 and 1, 2 and 3 g for coal 1, 2, and 3 respectively). The mixture was stirred under  $\text{N}_2$  overnight and the pentane was removed in vacuum over ca. 30-40 min. The flasks were heated slowly to  $100^\circ\text{C}$  until the  $\text{N}_2$  evolution ceased (20-30 min.; monitored with a bubbler) and then the temperature was raised to  $120^\circ\text{C}$  for an additional 30 min. After they were weighed the samples were stored under  $\text{N}_2$ . Approximately 0.4 g of these samples were extracted with

9:1 toluene:methanol in a Soxhlet extractor for 24 hr. and the extract was concentrated to about 1.5 mL by distillation through a 12 in. Vigreux column.

TGA analyses were done on 10-20 mg samples in an Ar or N<sub>2</sub> atmosphere. The temperature was programmed from 85°C to 1050°C at a rate of 20°C/minute. In general 5 runs were done on each sample.

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